REMARKS

Claim 1 has been amended. New claims 8 and 9 have been added. Thus, claims 1, 3, 4 and 6-9 are now pending in the present application. Support for the amendment to claim 1 may be found in the specification at page 24, last paragraph to page 26, line 7. Support for new claims 8 and 9 may be found in the specification at page 25, lines 13-17. Thus, no new matter has been added. Reconsideration and withdrawal of the present rejections in view of the comments presented herein are respectfully requested.

Prior art rejections

Claims 1, 3 and 7 were rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Chang et al. (US 7,120,342), and Claims 4 and 6 were rejected under 35 U.S.C. § 103(a) as being obvious over Chang et al., and further in view of Hiroshi et al. (JP 08-325401, and machine translation thereof). The Examiner contends that it would have been obvious to modify the process of Chang to form the composition into a sheet rather than a sheath since one of ordinary skill in the art would have found a change in shape to be obvious.

Claim 1 as amended recites that the compound that has a decomposing foamable functional group is a polymeric decomposing compound; and recites particular decomposing foamable functional groups. In accordance with the claimed process, a foamable composition is formed into a sheet having a thickness of 1 μm to 10 mm, and then irradiated with an active energy beam to foam the sheet. The foamable composition generates gases in the sheet due to a chain-reaction triggered by an acid or base, which is generated from the acid or base generator due to the action of the irradiated active energy beam. (*See, Polymer Engineering and Science*, Mid-December, 1983, Vol. 23, No. 17, pp. 953-956 (Exhibit A); and Polymers in Electronics, *Am. Chem. Soc. Symp. Ser.* 242, pp. 11-23, 1984 (Exhibit B).) The result of attacking the decomposing foamable functional group incorporated into the polymeric decomposing compound is that no low molecular weight residue remains in the formed foamed sheet. When such a low-molecular weight residue is absent in the sheet, bleed-out (a process in which the low-molecular weight residue appears on the surface of sheet when stored for a long period) is prevented, and excellent durability is exhibited. In addition, the decrease in glass-transition temperature is prevented, and therefore excellent thermal resistance is exhibited. Thus, the

presence of the recited decomposing foamable functional groups incorporated into the polymeric decomposing compound leads to the unexpected advantages listed above.

Chang et al. discloses a UV-curable and foamable resin composition containing a photopolymerizable urethane acrylate oligomer, a photopolymerable monomer, a photo polymerization initiator, a photolytic foaming agent selected from an azo compound, a combination of sulfonium salt and an inorganic carbonate, and a mixture thereof, and a photolysis catalyst. Thus, Chang et al. neither discloses nor suggests that a decomposing foamable functional group should be incorporated into the polymeric decomposing compound to form a foamed sheet, or that no low-molecular weight residue remains in the formed foamed sheet. In addition, these features are neither disclosed nor suggested by Hiroshi et al.

The unexpected advantages discussed above are neither disclosed nor suggested by Chang et al, either alone or in combination with Hiroshi et al., nor could these results have been predicted by one having ordinary skill in the art. Thus, these results strongly support the nonobviousness of the present claims.

Thus, claim 1, as well as claims 3, 4 and 6-9, which depend on claim 1, cannot be obvious over Chang et al. taken alone, or in combination with Hiroshi et al.

In view of the amendments and comments presented above, Applicants respectfully request reconsideration and withdrawal of the rejections under 35 U.S.C. § 103(a).

CONCLUSION

Applicants submit that all claims are in condition for allowance. However, should there be any questions concerning this application, the Examiner is respectfully invited to contact the undersigned at the telephone number appearing below.

Respectfully submitted,

KNOBBE, MARTENS, OLSON & BEAR, LLP

Dated: 9/14/09

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Possibilities for Photoimaging
Using Onium Salts

JAMES V. CRIVELLO

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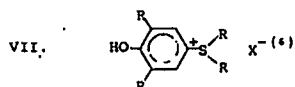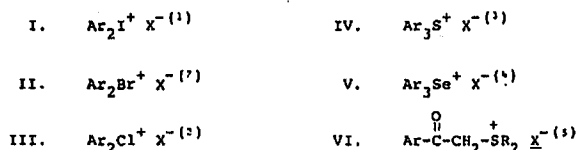*Schenectady, NY 12301*

The recent discovery that the photolysis of certain onium salts produces strong Brönsted acids presents a unique opportunity to design novel photoimaging systems based on these materials. For example, when used as photoinitiators, they can induce the negative image wise cationic polymerization of multifunctional epoxides, vinyl ethers, and lactones. Alternatively, they may be used to catalyze the degradation of hydrolytically sensitive polymers to give positive photoresists. The ability of still other onium salts to generate radical species as well as strong acids has been exploited to develop photoimaging processes which have no parallel in present photoresist technology. The processes consist of simultaneous radical polymerization and acid-induced cationic polymerization. Finally, the recent observation that the onium salts can be dye-sensitized allows them to be responsive to both the ultraviolet and visible regions of the spectrum and to be used with many commercial optical imaging systems.

INTRODUCTION

The recent nearly explosive growth in the electronics industry has been made possible through advances in photoresist technology. Originally developed for the printing industry over 50 years ago, photoresist technology has undergone extensive refinements to adapt it to meet the specific needs of the semiconductor industry. Further attempts to increase the density of microelectronic devices will stretch conventional optical photoresist technology to its limits of sensitivity, contrast, resolution, and etch resistance. At the same time, efforts are being made in many laboratories to develop new photoresist technology. This paper describes some recent developments in photochemistry from this laboratory which are uniquely suited to a wide diversity of photoresist applications.
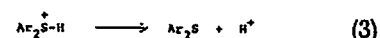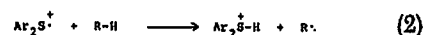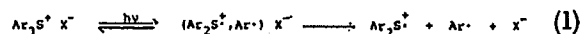
ONIUM SALT TECHNOLOGY

During the past few years we have reported that certain onium salts are very effective photoinitiators of cationic polymerization. The general structures of these onium salts are shown below.

I. $Ar_2I^+ X^-$ [1]

II. $Ar_2Br^+ X^-$ [7]

III. $Ar_2Cl^+ X^-$ [2]

IV. $Ar_3S^+ X^-$ [3]

V. $Ar_3Se^+ X^-$ [4]

VI. $Ar\text{-}\overset{O}{\underset{||}{C}}\text{-}CH_2\text{-}\overset{+}{S}R_2 \underline{X}^-$ [5]

VII. $HO\text{-}\langle\rangle\text{-}\overset{+}{\underset{R}{\overset{R}{S}}} X^-$ [6]

In this paper, we will limit our discussion to examples involving the triarylsulfonium salts (IV). These onium salts are typical of photoinitiators I–V with respect to their spectral absorption characteristics, quantum yields, and mechanism of photolysis. The photochemistry of onium salts VI and VII are considerably different and are discussed elsewhere (5,6).

Triarylsulfonium salts are especially attractive as photoinitiators in that they are rather easily prepared using a number of well established synthetic routes, and that structural modifications may be readily introduced to manipulate their spectral absorption characteristics (7). The mechanism by which these compounds undergo photolysis when exposed to ultraviolet light is shown in Scheme 1.

Scheme 1

$$Ar_3S^+ X^- \xrightarrow{h\nu} (Ar_2S^{+\cdot}, Ar\cdot)\ X^- \longrightarrow Ar_2S^{+\cdot} + Ar\cdot + X^- \quad (1)$$

$$Ar_2S^{+\cdot} + R\text{-}H \longrightarrow Ar_2\overset{+}{S}\text{-}H + R\cdot \quad (2)$$

$$Ar_2\overset{+}{S}\text{-}H \longrightarrow Ar_2S + H^+ \quad (3)$$

In the first step of the photolysis, homolytic cleavage of a carbon-sulfur bond occurs with the formation of a diarylsulfinium cation radical, an aryl radical, and an anion. Secondary radical fragments are produced by subsequent interaction of these species with the solvent or monomer, *R-H*. In addition to the radical products which are formed, a strong acid, *HX*, is generated when X^- is BF_4^-, PF_6^-, AsF_6^-, SbF^-, etc., which is responsible for initiating cationic polymerization.

James V. Crivello

The photolysis of triarylsulfonium salts is not quenched by oxygen or other singlet or triplet quenching agents. Photolysis rates have been shown to be highly dependent on the structure of the triarylsulfonium cation but independent of the structure of the anion. As expected, the photolysis rates are not influenced by temperature and exhibit a first power dependency on the intensity of irradiation (3).

Although simple triphenylsulfonium salts have their principal absorption at 230 nm in the deep UV, they and other triarylsulfonium salts can be readily photosensitized to respond to longer wavelength UV and to visible light (8-10). This feature of onium salt chemistry is particularly valuable in photolithography since it permits the photoimaging processes induced by these compounds to be optimally fitted to the specific irradiation source used for their exposure.

Although triarylsulfonium salt photoinitiators are efficiently photolyzed on irradiation, paradoxically they show little tendency toward thermal decomposition even when exposed to elevated temperatures (150°C) for long periods of time (1 to 2 hours). Radical photoinitiators on the other hand tend to be quite thermally labile in addition to being photosensitive. The high order of thermal stability observed with triarylsulfonium salts allows resists containing them to be subjected to long bake cycles without danger of premature degradation of their sensitivity.

PHOTOIMAGING PROCESSES BASED ON ONIUM SALTS
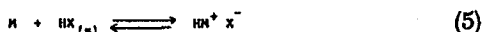
Cationic Polymerization

Triarylsulfonium salts and, in fact, all onium salts with structures I–VI can be considered latent photochemical sources of very strong protonic acids. When photolysis is carried out in the presence of a polymerizable monomer, M, protonation and subsequent polymerization occur as shown in Scheme 2.
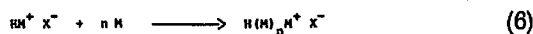
Scheme 2

Photolysis

$$Ar_3S^+ \; X^- \xrightarrow[\text{solvent-H}]{hv} Ar_2S + Ar-H + HX_{(s)} \quad (4)$$

Initiation

$$M + HX_{(s)} \rightleftharpoons HM^+ \; X^- \quad (5)$$

Propagation

$$HM^+ \; X^- + n \, M \longrightarrow H(M)_n M^+ \; X^- \quad (6)$$

Virtually all known types of cationically polymerizable monomers are polymerized using these photoinitiators. Included among these monomers are epoxides, cyclic ethers, mono- and polyfunctional vinyl compounds, spiroesters, spirocarbonates, and cyclic silicones. In general, photoinitiated cationic polymerizations are very facile at room temperature and are not inhibited by the presence of atmospheric oxygen. While they are adversely affected by the presence of gross amounts of water, trace quantities are well tol-

erated. Finally, mixtures of monomers together with photoinitiators have exceptionally long storage lives.

The above characteristics make photoinitiated cationic polymerizations ideal candidates for use in negative working resists. Several different photoresists have been fabricated based on these concepts.

The most successful of these resists have been those based on epoxy resins. A wide variety of different solid, liquid, cycloaliphatic, and aromatic containing epoxy resins are available from several commercial suppliers. When combined with an onium salt photoinitiator, surface active agents, and film forming additives, photoresists with excellent sensitivity can be obtained. Solid multifunctional novolac-epoxy resins are particularly attractive precursors for use in the fabrication of photoresists because the presence of multiple epoxide functionality in these resins enhances their apparent photoresponse.

$$\xrightarrow[Ar_3S^+ \; X^-]{hv} \quad (7)$$
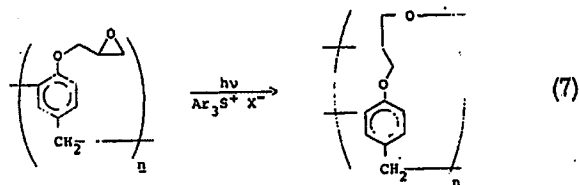
In addition, their adhesion to metallic and nonmetallic substrates alike is excellent and when crosslinked, they exhibit good swelling resistance to developing agents.

Monomers containing the vinyl ether functional group are more reactive than epoxy resins in onium salt photoinitiated cationic polymerization.

$$\xrightarrow[Ar_3S^+ \; X^-]{hv} \quad (8)$$
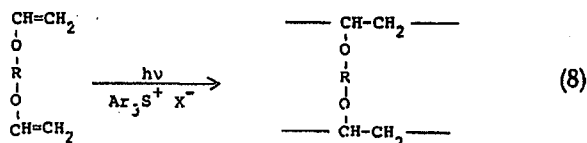
VII

A wide variety of desirable physical and chemical properties can be designed into these resins by varying the structure of R in VII. A series of negative photoresists with excellent photoresponse characteristics has been designed based on these materials.

Acid Catalyzed Condensation Polymerization

In addition to cationic polymerization, the strong protonic acids produced on photolysis of triarylsulfonium and other onium salts can be employed to carry out a wide variety of acid catalyzed condensation polymerizations. Typical of these reactions is the photoinduced condensation of melamine-formaldehyde resins as shown in *Eq 9*.

$$\xrightarrow[Ar_3S^+ \; X^-]{hv} \quad + \; H_2O \quad (9)$$
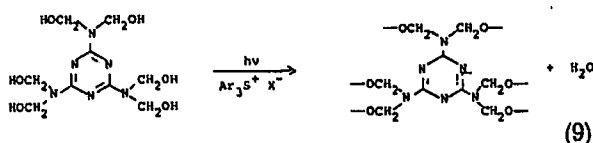
Similarly, resists based on urea and phenol formaldehyde resins can be patterned by image-wise exposure and are useful alone or in combination with epoxy resins for photoresist applications (14). Generally such resists require a postbake prior to development to complete the condensation and to enhance image formation.

Cationic Depolymerization

Many polymers containing heteroatoms in their main chain are known to undergo facile depolymerization when treated with an appropriate catalyst (15). This chemical principle has served as a basis for the design of a broad new class of positive working photoresists. For example, Saegusa and his coworkers have observed that polyethylene oxide is nearly quantitatively converted to dioxane when treated with a strong protonic acid at 10 to 40°C (16). A mechanism which explains this observation is shown in Scheme 3 and involves reinitiation followed by intrachain backbiting. The strong protonic acids provided by the photolysis of triarylsulfonium salts provide a means of selectively depolymerizing those portions of a photoresist film exposed to light. Dimeric species are the major products of these depolymerization reactions, although in some cases higher cyclic oligomers are also produced. In most cases, the cyclic oligomers have sufficiently low boiling points that they volatilize either during exposure or during a postbake cycle. This feature makes these photoresists unique in that no solvent is required for their development, i.e., they are "dry developable."

Scheme 3
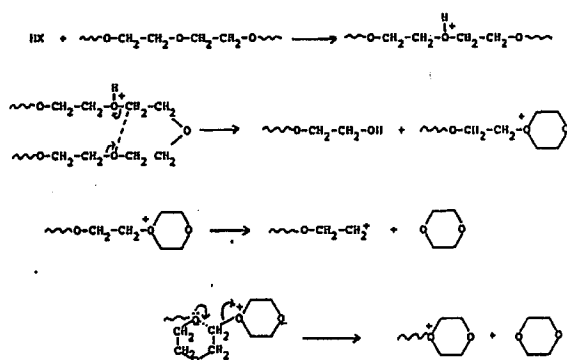
Acid Catalyzed Hydrolysis

It is well known that acids catalyze the hydrolysis of esters. When triarylsulfonium salts are incorporated into a film of a hydrolytically sensitive polycarbonate and exposed to ultraviolet irradiation, the acid which is produced catalyzes chain scission at random sites along the backbone (Eq 10).

$$(10)$$
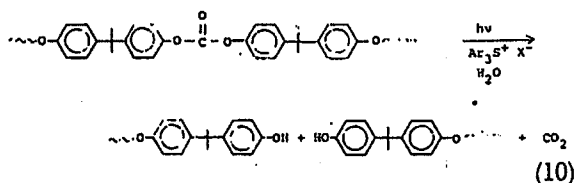
Usually, water absorbed by the polymer or present as atmospheric moisture is sufficient to produce effective cleavage. Other parameters which control the extent of hydrolytic chain cleavage and, therefore, the sensitivity of the resist are the catalyst level, the time between exposure and development, and whether or not a postbake prior to development is used. During development, one takes advantage of the higher dissolution rate of the degraded polymer vis-à-vis the intact polymer to generate a positive image of the mask. This concept is general in its application and has been extended to produce positive resists using a number of polyesters, polycarbonates, polysulfonates, polyacetals, and polyazomethines.
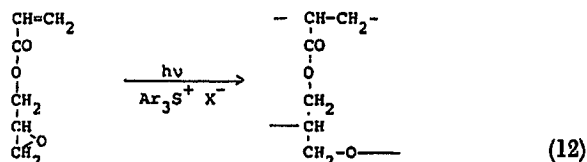
Radical Polymerizations

As shown in Scheme 1, the photolysis of triarylsulfonium salts produces in addition to strong protonic acids, a variety of radical fragments. Triarylsulfonium salts are, thus, capable of photoinitiating free radical polymerizations.

$$(11)$$
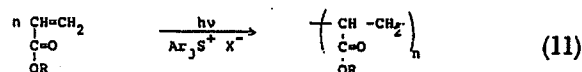
Furthermore, these salts have as an added advantage that compared to conventional free radical photoinitiators, they exhibit excellent thermal and dark stability. In fact, triarylsulfonium salts have been employed as inhibitors to prevent the spontaneous free radical polymerization of unsaturated polyesters (18). Yet, when these same compounds are exposed to UV light in the presence of vinyl monomers, rapid polymerization is observed. A considerable number of mono- and polyfunctional vinyl monomers are commercially available and can be employed for the fabrication of photoresists.

Simultaneous Radical and Cationic Polymerizations

Simultaneous radical and cationic polymerizations can be carried out with the aid of triarylsulfonium salt photoinitiators (18–20). These polymerizations can proceed independently of one another as when both free radical and cationically polymerizable monomers are present. Such systems are known as interpenetrating networks. Alternatively, monomers, for example glycidyl acrylate, which have both types of polymerizable groups present in the same molecule, may be used to give cross-linked networks useful as negative working resists.

$$(12)$$

Simultaneous radical and cationic photoinitiated polymerizations are superior to free radical photoinitiated polymerizations alone for photoresist applications because they are extremely rapid and exhibit greatly-reduced oxygen inhibition effects. Fur-

James V. Crivello

ther, such hybrid systems can provide a broader spectrum of resist materials whose critical properties such as photoresponse, adhesion, plasma resistance, film forming characteristics, etc., can be modified by judicious choice of combinations of both types of monomer substrates.

Simultaneous Radical and Acid Catalyzed Condensation Reactions

Another class of hybrid systems with considerable potential application as photoresists are simultaneous free radical and acid catalyzed condensation polymerizations. *Equation 13* illustrates one such system which has been explored in our laboratory. Aqueous

$$(13)$$
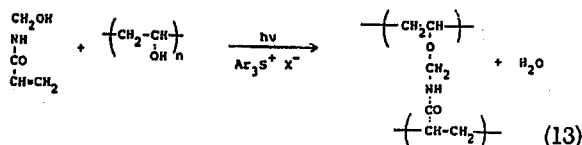
polyvinyl alcohol solutions containing 5 to 20 percent N-methylolacrylamide and a triarylsulfonium salt are film cast onto a substrate and dried. On irradiation, the free radical polymerization of the N-methylolacrylamide proceeds rapidly.

Simultaneously, the two polymers undergo acid catalyzed crosslinking through the alcohol and methylol groups with the elimination of water. These photoresists are especially attractive since they are inherently low in cost, exhibit good photosensitivity, and can be developed in neutral aqueous solutions. These systems, like the others described in this paper, can be dye sensitized to broaden their response to both long wavelength UV and to visible light.

Polymers Containing Photoactive Onium Salts in Their Backbones

The observation that onium salts undergo efficient photolytic fragmentation suggests that if such moieties were included in the backbone of a polymer, the polymer would suffer degradation on irradiation. Recently, we have described the preparation of such a polymer based on diaryliodonium salt chemistry (*Eq 14*) (22).

$$(14)$$
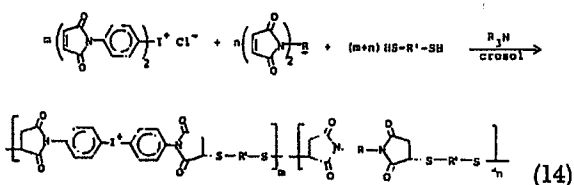
Using this synthesis, a series of film forming polymers were prepared which function as positive working resists. Approximately 10 percent of the repeating units are required to have the photosensitive iodonium salt groups present for useful photoresist properties to be achieved. Similarly, the introduction of appropriate functional groups into other photosensitive onium salts would allow them to be incorporated into polymers in an analogous manner. One can envision numerous opportunities for the design of new photoresists based on this concept.

SUMMARY

The prospects for the design of new positive and negative photoresists based on onium salt chemistry are very bright. In this paper, an attempt has been made to present only a few selected examples based on our investigation of eight new imaging systems in which photosensitive onium salts play integral roles. Doubtless, the reader can supply many more workable systems based on the concepts outlined here.

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2

Applications of Photoinitiators to the Design of Resists for Semiconductor Manufacturing

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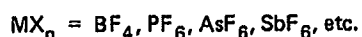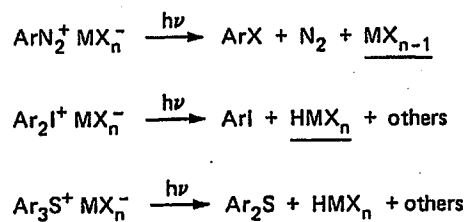IBM Research Laboratory, San Jose, CA 95193

Acids generated via radiolysis of cationic photoinitiators, such as aryldiazonium, diaryliodonium, and triarylsulfonium metal halides can induce a variety of chain reactions in polymers, including (1) cross-linking, (2) catalytic deprotection, and (3) catalytic depolymerization. All of these reactions can be exploited in the design of resist materials. When formulated with the onium salt photoinitiators, (1) epoxy resins undergo efficient cross-linking reactions to provide negative tone resists; (2) poly(p-t-butoxy carbonyloxystyrene) is converted to poly(p-hydroxystyrene) in the exposed areas to provide either a positive or negative resist tone depending on the developer employed; and (3) polyaldehydes are completely reverted to monomer upon exposure and vaporize during the exposure to provide self-developing positive resists. The extremely high sensitivity of these systems is achieved through *chemical amplification*.

The continuing trend toward higher circuit density in microelectronic devices has motivated research efforts in a variety of high resolution lithography techniques, including electron beam, x-ray, and deep UV (200-300 nm) technologies. Each of these new technologies demands a highly sensitive resist system in order to be of practical use. We have sought resist systems designed to meet the high sensitivity requirements of these microlithography techniques, and have found that certain cationic photoinitiators provide a basis for the design of several such systems. These systems achieve their high sensitivity as a result of designing the polymer matrix to provide *chemical amplification* of the initial photoreaction.

In each system, the primary photo-event is dissociation of the cationic photoinitiator to produce an acid. This reaction proceeds with a quantum efficiency that is characteristic of the particular initiator. The photogenerated acid then interacts with a carefully chosen polymer matrix to initiate a chain reaction, or acts as a catalyst, such that a single molecule of photogenerated acid serves to initiate a cascade of bond making or breaking reactions. The effective quantum efficiency of the overall process is the product of the photolysis reaction efficiency times the length of the chain reaction (or the catalytic chain length). This multiplicative response constitutes

gain or *chemical amplification* of the initial photo-event and provides for very high effective quantum efficiency (1-5).

The acid generating photoinitiators that provide the basis for our studies are onium salts that have been described in the work of Schlesinger (6,7) and Watt (8) and by Crivello (9) who pioneered their use as initiators for photocuring of coatings. The initiators include aryldiazonium salts that generate Lewis acids upon photolysis and diaryliodonium and triarylsulfonium salts that generate strong Bronsted acids (Scheme 1).

$$ArN_2^+ MX_n^- \xrightarrow{h\nu} ArX + N_2 + MX_{n-1}$$

$$Ar_2I^+ MX_n^- \xrightarrow{h\nu} ArI + HMX_n + others$$

$$Ar_3S^+ MX_n^- \xrightarrow{h\nu} Ar_2S + HMX_n + others$$

MX_n = BF_4, PF_6, AsF_6, SbF_6, etc.   Scheme 1. Photochemistry of onium salts.

The acids that are generated by photolysis of these salts have been exploited in the cross-linking of polymers and oligomers containing oxirane or thiirane rings (6-12). Very sensitive, negative tone resists have been developed on the basis of these reactions (13). We have found that these photogenerated acids are also capable of catalyzing the scission of carbon-heteroatom linkages in certain polymers. These cleavage reactions have been utilized to design both positive and negative resists.

Results and Discussion

Negative Mode (Cross-linking). Dubois et al. (13) have described the preparation of a sensitive negative resist based on onium salt sensitization of copolymers of 2,3-epithiopropyl methacrylate and methyl methacrylate and Crivello and co-workers have used a similar reaction to generate low resolution images in epoxy resins (14). The sensitivity of these systems derives from the chain reaction character of the ring opening polymerization (cross-linking) that is responsible for their function. This is an example of chemical amplification. We were therefore tempted to explore high resolution image generation in epoxy resins.

Celanese Epi-Rez SU-8 was chosen for these studies. This resin is a polyfunctional epoxy novolac resin (Scheme 2) made from bisphenol-A. It is optically
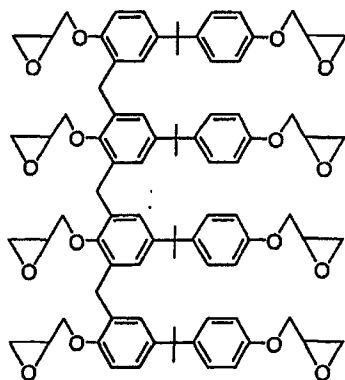
Scheme 2. Epi-Rez SU-8 (Celanese).

dense and strongly absorbing below 300 nm hence, we chose diazonium salts that absorb above 300 nm as initiators. *p-n*-Hexyloxybenzenediazonium metal halides were prepared for this purpose. They have an absorption maximum near the high intensity 313 nm mercury emission with $\varepsilon = 12,000-17,000$ and are soluble in organic solvents that will also dissolve SU-8. The SU-8 resin (4 g) was dissolved in 2-butanone (6 ml) to which was added the diazonium hexafluorophosphate (0.2 g). Resist films were prepared by spin coating the resulting solution on silicon wafers. The films were baked at 85° for 10 minutes to give 6 μ thick coatings. Because the diazonium salt begins to undergo thermolysis at 97°C (TGA), the baking conditions had to be carefully controlled. The onium salt-epoxy resist films were exposed through a patterned mask to 313 nm radiation, then developed in a mixture of $CHCl_3$ and hexanes (2:1 by volume) for 90 seconds, rinsed with hexanes for 10 seconds, then with CH_2Cl_2 for 15 seconds. Scanning electron micrographs of the resulting negative resist patterns are provided as Figure 1.

The patterns generated in the SU-8 resist show excellent image quality and slightly undercut profiles. However, the swelling phenomena that always occur during the development of negative resists which function on the basis of cross-linking reactions became apparent in smaller features, and limit the resolution of this system. The lower resolution limit depends on film thickness, developer and rinse composition, and on a variety of other process variables. No attempt was made to determine the ultimate resolution limits of the system but, it is clearly possible to generate images with minimum features in the 1 to 2 μ range with aspect ratios near 1.
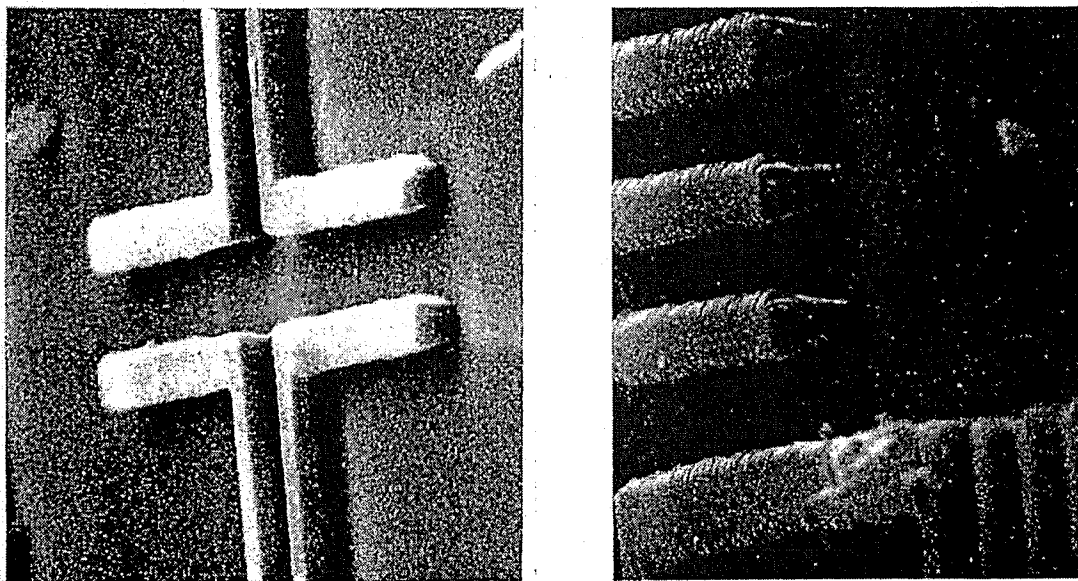


Figure 1. Negative patterns in SU-8.

<u>Positive</u> or <u>Negative Mode</u> (<u>Catalytic Deprotection</u>). We have recently focussed our attention on the design of positive tone resist systems that incorporate chemical amplification. One such new class of positive resist materials is based on the photochemical generation of a substance that catalyzes the cleavage of polymer pendant groups. Here, the effective quantum efficiency of the system is the product of the quantum yield of the photochemical event and the number of side chain transformations achieved by one molecule of the catalyst. This multiplicative response constitutes gain of the sort we seek. One polymer upon which the new system can be based is poly(p-t-butoxycarbonyloxystyrene) (PBOCST) (<u>15</u>) (Scheme 3). The initiators for this system are again various onium salts that undergo efficient photolysis to produce strong acids.

PBOCST is thermally stable to ca. 200°C. Above 200°C, the polymer loses about 45% of its weight as carbon dioxide and isobutene (<u>15</u>). Diphenyliodonium and triphenylsulfonium hexafluoroarsenates are thermally stable to ca. 250° and 300°, respectively. (<u>16,17</u>) Consequently, the resist formulated from PBOCST and these salts is stable to the baking conditions required for formation of high quality spin coated films, and the formulations have a long shelf life when stored at room temperature under yellow light.

The t-butoxycarbonyl group (t-BOC) and t-butyl esters have been widely employed as protecting groups in peptide synthesis (<u>18</u>). These structures are labile toward strong acids. In fact, while studying the cationic polymerization of p-t-butoxycarbonyloxy-α-methylstyrene, we noticed that a substantial amount of the t-BOC protecting group was cleaved during polymerizations initiated with BF_3OEt_2 or PF_5 (<u>19</u>). This acidolysis reaction can be conveniently monitored by either UV or IR spectroscopy.

Figure 2a shows the IR spectrum of a 1 μ thick PBOCST film containing 20% w/w of diphenyliodonium hexafluoroarsenate. The film was prepared by spin coating and was then baked at 100°C for 30 minutes. The thermal stability of the resist system is evidenced by the observation that no measurable phenolic hydroxyl band is generated during the baking process. After exposure to UV light, only a slight spectral change is observed, indicating that exposure alone is not an efficient means of deprotection. However, upon baking the exposed film at 100° for one minute, the reaction was brought to completion as evidenced by disappearance of the characteristic t-BOC carbonyl band at 1755 cm^{-1} and the appearance of a strong phenolic OH stretching absorption (Figure 2c). The deprotection reaction can also be followed by UV spectroscopy since the long wavelength absorption band of poly (p-hydroxystyrene) (PHOST) is both more intense and red shifted from its precursor, PBOCST (Figures 3 and 4). The acid produced by photolysis of the onium salt catalyzes thermolysis (acidolysis) of the t-BOC group via an A_{AL}-1 type mechanism (<u>20</u>). The reaction is slow at room temperature but very fast at 100°C, a temperature well below that required to thermolyze the protecting group in the absence of an acid catalyst. It should be noted that the photogenerated acid is not consumed in the t-BOC cleavage reaction. It serves only as a catalyst. Therefore, one mole of acid can cleave many t-BOC side chain groups, thus providing the desired chemical amplification of the initial photoreaction.

After exposure and post baking, the exposed areas of the t-BOC resist films are converted into PHOST. This is a polar, even acidic polymer that is soluble in a range of polar solvents such as alcohols or aqueous base, in which the precursor, PBOCST, is totally insoluble. Conversely, PBOCST is soluble in many nonpolar, lipophilic solvents in which the phenolic PHOST is insoluble. This large change in polarity that results
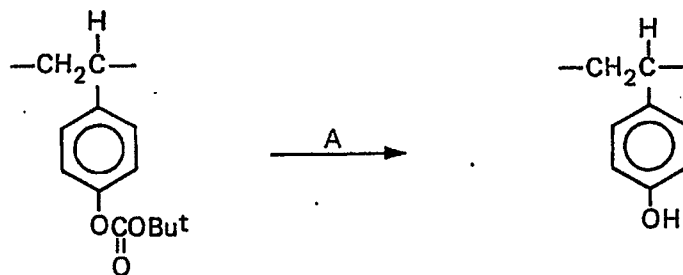
Scheme 3. Acidolysis of PBOCST.
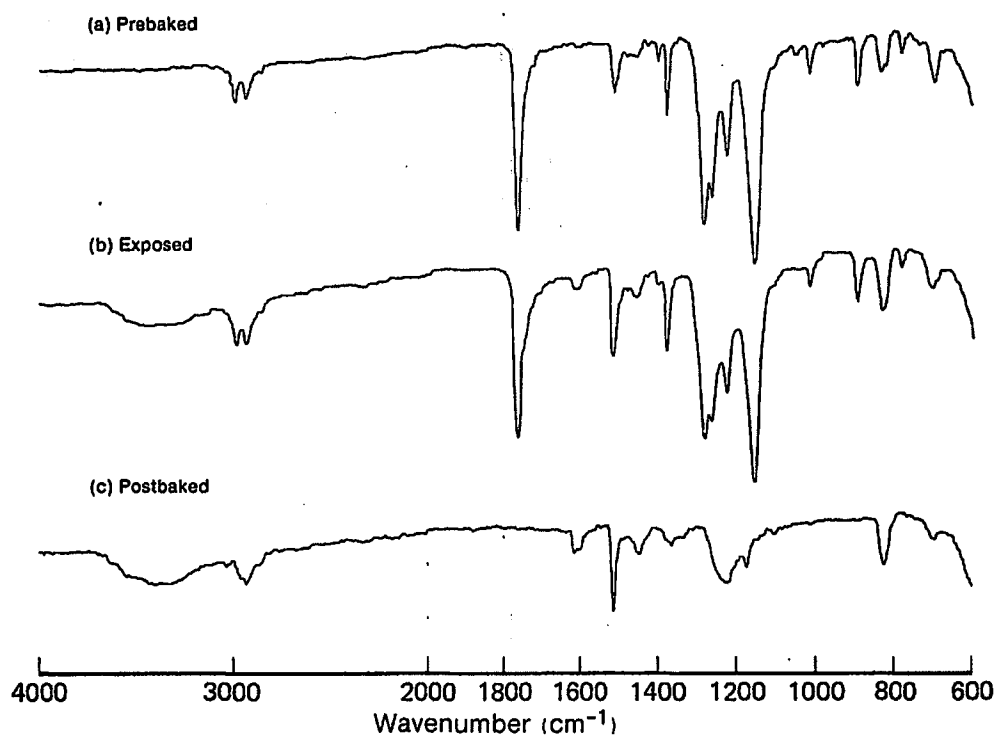
Figure 2. IR spectra of PBOCST/Ph_2IAsF_6: (a) before exposure, (b) after exposure, and (c) after postbake.
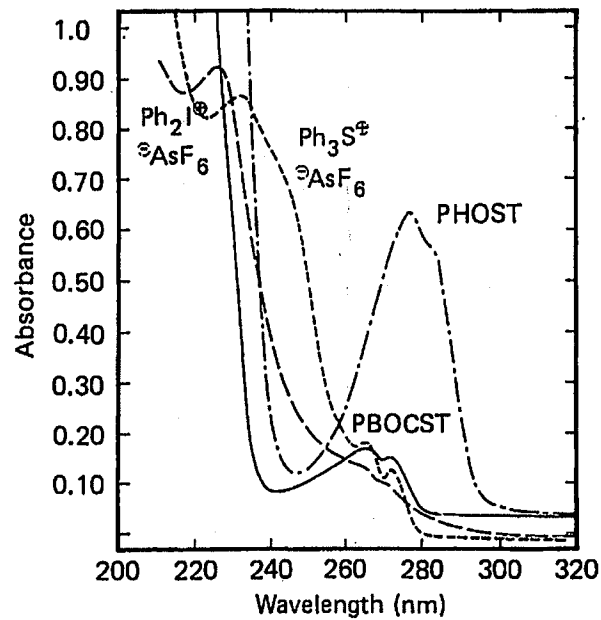
Figure 3. UV spectra of Ph_2IAsF_6, Ph_3SAsF_6, PBOCST, and PHOST.
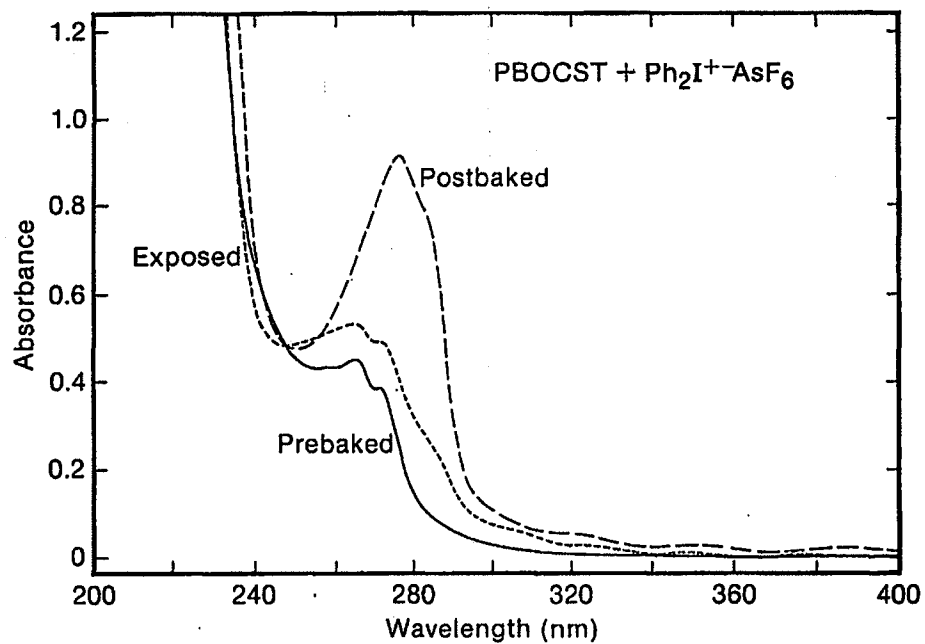

Figure 4. UV spectra of $PBOCST/Ph_2IAsF_6$ before and after exposure and after postbake.

from exposure and baking allows the exposed films to be developed either as negative or positive resists. Use of a nonpolar developer selectively dissolves the unexposed (PBOCST) areas of resist films to give negative tone images. Development with a polar solvent selectively dissolves the exposed (PHOST) areas of the films to give positive tone images. The solubility differentiation in the system is solely dependent on a change in the polarity of the repeating units, and thus its mechanism of action is quite different than that of either the familiar positive tone resists based on dissolution inhibitors, such as the diazonaphthoquinone/novolac systems, or resists that funcion on the basis of polymer main chain scission reactions, such as PMMA or the cross-linking negative systems. Since the phenolic, PHOST polymer is totally insoluble in solvents that dissolve PBOCST, negative tone images in this new resist do not suffer from resolution limitations due to swelling. No evidence of swelling is observed in either the positive or negative tone developers.

Resist systems that function on the basis of a change in the polarity of a side chain are few, and none apparently suffer from swelling phenomena. IBM researchers have reported a negative resist system that presumably functions on the basis of insolubilization by salt formation. This system is based on alkyl halide sensitized films of polystyrene bearing tetrathiofulvalene pendant groups (21). We have reported that poly(*t*-butyl methacrylate) is converted to poly(methacrylic acid) by reaction with acids generated via photolysis of onium salts (1,4) and recently, Hatada et al. reported a related system in which poly(α,α-dimethylbenzyl methacrylate) is transformed into poly(methacrylic acid) upon e-beam radiation which allows aqueous base development (22). In none of these cases is there reported any evidence of swelling during development.

The absorbance spectra of PBOCST and PHOST are provided as Figure 3. PBOCST is very transparent at 240-300 nm. The iodonium and sulfonium salts both absorb significantly in this spectral region but do not absorb significantly above 300 nm. Consequently, the PBOCST-onium salt resist is ideally suited to deep UV lithography (23). The resist can, however, be sensitized to longer wavelength through incorporation of dyes. The effect of polynuclear aromatics has been studied by Crivello (24,25) and by Pappas (26). These compounds have proven to be effective in the PBOCST system. Sensitization of resist formulations based on iodonium salts with pyrene renders them sensitive in the mid-UV (313 nm), and addition of perylene provides sensitivity in the near UV (365, 404, 436 nm). Figure 5 documents the conversion of PBOCST to PHOST by perylene sensitization of diphenyliodonium hexafluoroarsenate to 365 nm radiation. Preliminary investigations have shown that the PBOCST-onium salt systems are also sensitive to electron beam exposure. We have also demonstrated that polymers containing *t*-butyl ester side chains can be imaged via incorporation of onium salts. These include poly(*t*-butyl methacrylate), poly(*t*-butyl *p*-vinylbenzoate) and poly(*t*-butyl *p*-isopropenylphenyloxyacetate).

We have succeeded in producing excellent, high resolution images in the PBOCST-onium salt, deep UV resists. Films of PBOCST (M_n 30K) containing 20 wt% of diphenyliodonium hexafluoroarsenate were spin coated on silicon wafers from cyclohexanone then baked at 100° for 30 minutes to provide striation free 1.25 μ thick films. The resist was exposed through a quartz mask and a narrow band width, 254 nm filter using an Oriel Associates Inc. Model 780, Hg-Xe lamp. The films were baked at 100° for 10 seconds following exposure. Positive images were obtained by development in a mixture of Shipley MF 312 (aqueous tetramethylammonium hydroxide solution) and water (1:1 by volume) (Figure 6a) and negative images were produced by development in a mixture of CH_2Cl_2 and hexane (2:1 by volume) (Figure 6b). Other positive developers, such as Shipley AZ 2401 and isopropanol, work equally well.
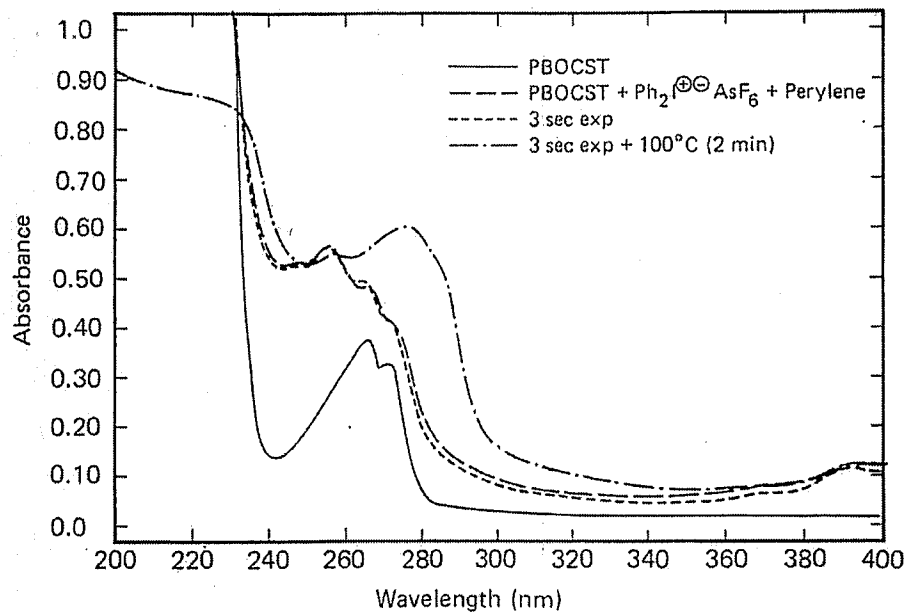
Figure 5. UV spectra of PBOCST/Ph$_2$IAsF$_6$/Perylene before and after exposure to 365 nm radiation and after postbake.
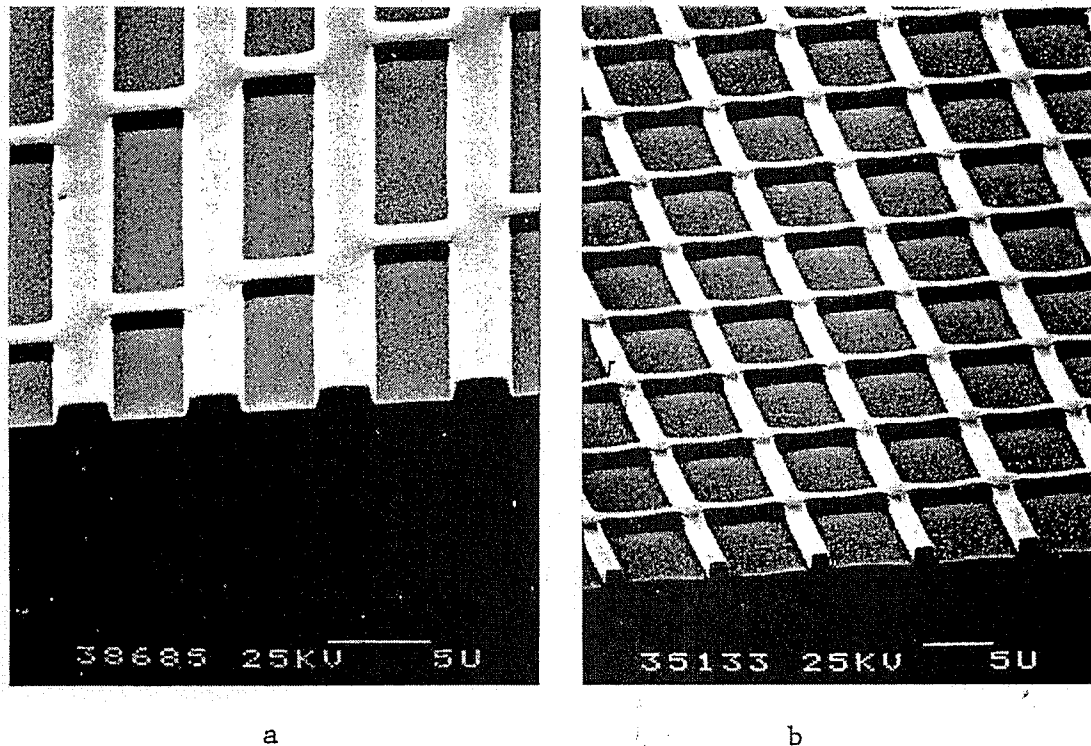

a   b

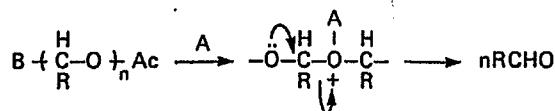Figure 6. Positive (a) and negative (b) images in PBOCST/Ph$_2$IAsF$_6$.

Positive <u>Mode</u> (Catalytic <u>Depolymerization</u>). In the conceptual design of these systems, amplification is achieved by choosing polymers, which, when subjected to a single radiation induced bond scission, undergo a spontaneous depolymerization that results in complete reversion to monomer. The polymers upon which the new system is based are polyaldehydes. Aldehydes undergo anionic or cationic polymerization in a reversible, equilibrium reaction. Many of these systems have ceiling temperatures well below room temperature such that the polymerization must be carried out at cryogenic temperatures, and if the polymer is isolated, it rapidly depolymerizes to monomer. If, however, these polymers are end-capped by acylation or alkylation prior to isolation, they are often quite stable. Vogl et al. have extensively and intensively studied the equilibrium polymerization of aliphatic aldehydes (<u>27</u>). Most of these materials are intractable, insoluble substances because of their high crystallinity. Certain aromatic dialdehydes, such as phthalaldehyde and *o*-formylphenylacetaldehyde undergo cyclopolymerization with a ceiling temperature of approximately −40°C (<u>28,29</u>). After end-capping, these aromatic polyacetals are stable to 180°C, as evidenced by TGA analysis and, unlike their aliphatic counterparts, are soluble in common organic solvents. We have found polyphthalaldehyde to be particularly useful for our systems (Scheme 4).
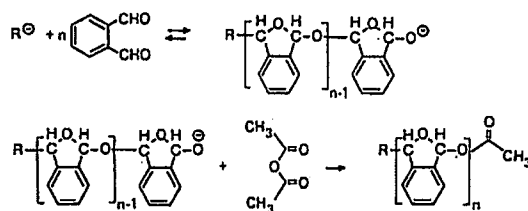
Scheme 4. Anionic polymerization of phthalaldehyde.

There have been earlier reports of the utility of polyaldehydes as imaging media. Solvent development of e-beam exposed polyphthalaldehyde has been reported (<u>30</u>). Aliphatic polyacetals with photosensitive end groups have been investigated as a photoimaging system in which the aldehyde monomer released from a polyacetal upon radiation followed by heating is used to cross-link certain polyamides (<u>31</u>). Sensitization of polyphthalaldehyde by addition of substances which generate acids upon radiation such as poly(vinyl chloride) or phenol derivatives has also been applied to an imaging technology on the basis of changes in optical density (<u>32,33</u>) and used as resist materials that produce images by heating and/or solvent development after exposure (<u>34</u>).

We have reported that unsensitized polyphthalaldehyde undergoes partial depolymerization when exposed to deep UV or e-beam radiation and that the sensitization of polyphthalaldehyde by copolymerization with *o*-nitrobenzaldehyde provides about 50% dry development upon heating after deep UV irradiation (<u>3,5</u>). Subsequently Hatada et al. reported that copolymers of aliphatic aldehydes are depolymerized to monomeric aldehydes upon exposure to e-beam or x-ray to provide highly sensitive self-developing positive resists (<u>35</u>). We have studied the sensitization of polyphthalaldehyde through incorporation of the onium salt photoinitiators in hope of achieving catalytic acidolysis of the acid-labile main chain acetal bonds (Scheme 5), a reaction of the sort observed by one of the authors (H.I.) during polymerization of anhydrosugars by reaction with the cationic initiator PF_5 at cryogenic temperatures (<u>36</u>). As expected, addition of triphenylsulfonium or diphenyliodonium hexafluoroarsenate (10 wt% to the polymer) has allowed imaging of 1 μ thick films of polyphthalaldehyde at 2-5 mJ/cm² of 254 nm radiation and at 1.0 μC/cm² of

$$B \left(\begin{array}{c} H \\ | \\ C-O \\ | \\ R \end{array} \right)_n Ac \xrightarrow{A} \quad -\overset{H}{\underset{R}{O-C}}-O-\overset{\overset{A}{|}}{\underset{R}{C}}- \longrightarrow nRCHO$$

Scheme 5. Acidolysis and depolymerization of polyphthalaldehyde.

20 keV e-beam radiation. Clean relief patterns with resolution below 1 μ line width are generated by exposure alone even without heating. No development step is required.

In a typical experiment, polyphthalaldehyde was dissolved in bis-(2-methoxyethyl) ether or cyclohexanone, to which was added the onium salt at 10 wt% to the polymer. Films spin coated on Si wafers were baked at 100°C for 10 minutes and then image-wise exposed. Optical micrographs of the resist images generated upon UV, e-beam, and x-ray radiations are exhibited in Figures 7a, b, and c, respectively.

The UV sensitivity of the polyphthalaldehyde-onium salt system is dependent on the concentration and structure of the onium salts. At 10 wt% loading the sensitivity to narrow band width 254 nm radiation is 1-7 mJ/cm^2 and is insensitive to the structure of the salts. However, at 2 wt% loading of triphenylsulfonium or diphenyliodonium hexafluoroarsenates or p-hexyloxybenzenediazonium tetrafluoroborate much higher doses are required to achieve self-development and the sensitivity decreases with the salt structures in the sequence listed.

Formation of monomeric phthalaldehyde due to acidolysis and depolymerization of polyphthalaldehyde initiated by the photolysis of onium salts is clearly demonstrated by IR spectroscopy (Figure 8). Figure 8c shows vaporization of the aldehyde monomer upon heating. The monomeric phthalaldehyde is crystalline at room temperature but sublimes under vacuum without heating. We have successfully delineated self-developed images in a 2.8 μ thick film at a dose of 1.0 μC/cm^2 of 20 keV e-beam radiation, which were subsequently transferred to silicon oxide by treatment with either buffered HF or CF$_4$/O$_2$ plasma.

Dry developing resist materials that require no post-exposure development involving solvents have been sought for some time (37-41). The interest in such materials throughout the semiconductor industry stems from the potential they provide for higher throughput and higher device yields. The higher yields result from both the reduction in process steps and the fact that such materials provide the potential for carrying out exposure, development, and pattern transfer under high vacuum, thereby reducing the number of defects due to atmospheric contaminants and the development process. The polyphthalaldehyde/onium salt system is one of only two resists of which we are aware that undergo clean self-development without the need for post-exposure processing of any kind. The other resist is based on the copolymers of aliphatic aldehydes and was recently reported by Hatada et al. (35).

We are continuing to explore the limits of the PBOCST and polyphthalaldehyde resist systems, as well as other materials that incorporate chemical amplification.

Experimental

Materials. The epoxy resin used for the negative patterning was Epi-Rez SU-8 purchased from Celanese. Poly(p-t-butoxycarbonyloxystyrene) (PBOCST) was synthesized by radical polymerization of p-t-butoxycarbonyloxystyrene (BOCST), as described by Frechet et al. (15). Phthalaldehyde purchased from Aldrich Chemical Company was purified by recrystallization from CH$_2$Cl$_2$-hexanes and polymerized by
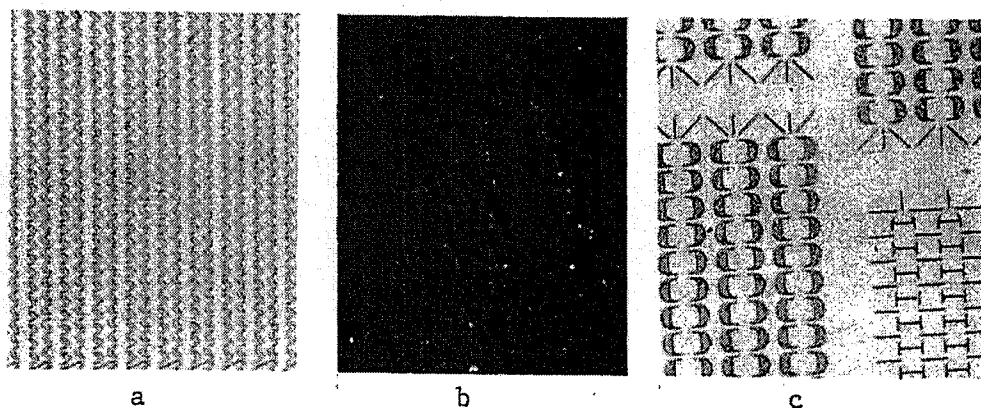
a   b   c

Figure 7. Self-developed images in polyphthalaldehyde: (a) 254 nm deep UV, Ph_3SAsF_6, (b) 20 keV e-beam, Ph_3AsF_6, and (c) Al-Kα x-ray, Ph_2IAsF_6.

(a) Prebaked

(b) Exposed

(c) Postbaked

4000   3500   3000   2500   2000   1800   1600   1400   1200   1000   800   600
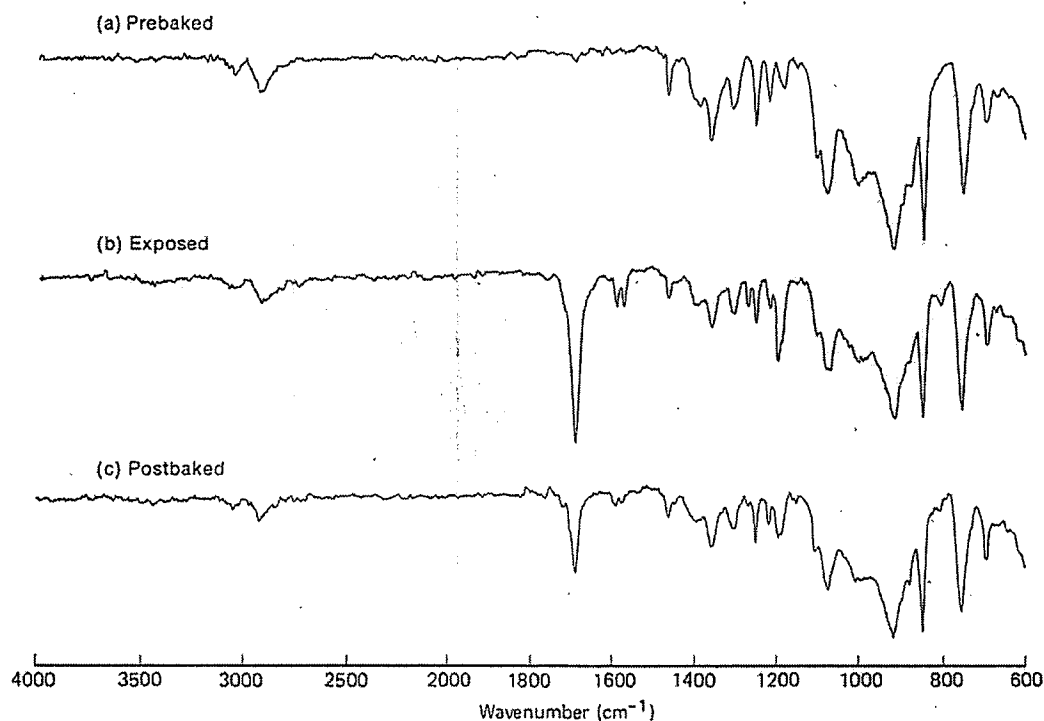
Wavenumber (cm^{-1})

Figure 8. IR spectra of polyphthalaldehyde/Ph_2IAsF_6 before and after exposure to 254 nm radiation and after postbake.

anonic initiation with n-butyllithium, phenylmagnesium bromide, or potassium t-butoxide/18-crown-6 in THF at $-78°C$ under high vacuum with use of a break-seal technique. The phthalaldehyde polymerization was terminated by adding a cold mixture of acetic anhydride and pyridine at $-78°C$ to end-cap the polymer. The end-capped polymers are of high molecular weight (M_n=35,000-54,000 and M_w=43,000-100,000), stable to ca. 180°C, according to TGA analysis, soluble in common organic solvents, and can be spin cast from solution to provide clear,

isotropic, noncrystalline films. The synthesis of the onium salt photoinitiators has been well documented in the literature (6-12).

Measurements. IR spectra were recorded on a Perkin Elmer 283 spectrometer and UV spectra on a Hewlett Packard Model 8450A UV/VIS spectrophotometer. Molecular weight measurements were made using a Wescan 230 or 231 recording membrane osmometer with toluene or THF as solvent while GPC measurements were made on a Waters Model 150 chromatograph equipped with six or eight μstyragel columns at 30° or 40°C in THF. TGA analyses were performed on a DuPont 951 or 1090 at a heating rate of 10°C/min.

Lithography. Electron beam exposures were carried out with an IBM vector scan e-beam exposure tool at 20 keV. X-ray exposures were carried out under vacuum by Al-Kα radiation, and UV exposures with a Cannon PLA 500, Oriel illuminator, Hybrid Technology Group Model 345-10, or Optical Associates Inc. Model 780 in contact mode.

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